Silver Filled Carbon Nanotubes used as Spectroscopic Enhancers

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We analyse from a theoretical point of view the optical properties of arrays of carbon nanotubes filled with silver. Dependence of these properties on the different parameters involved is studied using a Transfer Matrix formalism able to work with tensor-like dielectric functions and including the full electromagnetic coupling between the nanotubes. We find these structures exhibit very strong linear optical response and hence could be used as spectroscopic enhancers or chemical sensors in the visible range. Very localised surface plasmons, created by the electromagnetic interaction between the capped silver cylinders, are responsible of this enhancing ability. Enhancements of up to 10^6 in the Raman signal of molecules absorbed on these arrays could be obtained.

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The so called coinage metals (Au, Ag and Cu) exhibit very strong linear and non-linear optical response when they are structured on the nanometre scale. Their ability to enhance optical fields has been widely used in the last twenty years to study spectra of several molecules, taking advantage of the Surface Enhanced Raman Scattering (SERS) effect [1]. This effect appears on suitably rough metal surfaces of Au, Ag or Cu and is connected with excitation of very localised surface plasmons present in the vicinity of highly coupled metal features [2]. However, controlled use of coinage metals as spectroscopic enhancers has proven to be very difficult, due to the absence of well-defined, stable macroscopic materials made of them, and various approaches to preparation of ordered arrays of metal nanoparticles have been reported only very recently [3]. Basically, these techniques consist of capping the nanoparticles with organic molecules of different sizes in order to control the interparticle separation.

Carbon nanotube technology is another promising new area in materials science [4]. Multishell nanotubes made of a number of concentric cylinders of planar graphite with diameters ranging from 2 to 25 nm and lengths of up to several microns have now become available. One of the most interesting applications of these nanometre size tubes is linked to their hollow character: carbon nanotubes could be used as nanoscale moulds. Filled nanotubes can be synthesised by capillary action [5] or by using composite anodes in the arc discharge [6], resulting in formation of encapsulated compounds or elongated nanostructures of different materials (carbides, oxides, organic solvents or even pure metals). Very recently it has been possible to fill carbon nanotubes with a coinage metal like silver, using capillary forces [7]. On the other hand, bulk alignment of nanotubes has been also reported using different techniques [8,9]. In these ordered arrays the carbon nanotubes form very close-packed structures.

The aim of this letter is to propose a scenario that combines both areas of materials science. We investigate the optical response of arrays of Ag-filled carbon nanotubes in order to see if the capacity of silver nanostructures to enhance optical fields is retained when they are encapsulated inside carbon nanotubes. If so, these well-defined structures could have important optical applications as, for example, spectroscopic enhancers or chemical sensors in the visible range.

Our model for an array of Ag-filled carbon nanotubes is displayed in figure 1. The tubes are infinitely long in the z direction and form a periodic structure in the x direction. In accordance with experimental evidence [7,9], the outer diameter of the nanotubes is chosen to be $d_{out} = 10$ nm and the distance between them, d, 10.3 nm (close-packed structure). It has been reported that only tubes with inner diameters of 4 nm or more can be filled with silver using capillary forces, and the distribution of inner diameters is broad varying from 4 to 9 nm [7]. Bearing this in mind, the diameter of the encapsulated silver tubules, d_{in}, will be varied in our calculations between 3 and 9.5 nm, in order to study dependence of the optical response of these arrays on the diameter of the inner core. Since the outer diameter of the tubes and the distance between them are fixed, varying d_{in} changes the separation between metal nanoparticles.

We consider an electromagnetic p-polarised plane wave of frequency ω and momentum $\mathbf{k}$ normally incident on the structure, and we analyse its interaction with an array of carbon nanotubes. For this polarisation, the incident $\mathbf{E}$ field is perpendicular to the axis of the tubes and surface plasmons of the nanotubes can be excited. In particular, we calculate the optical reflectance, $R(\mathbf{k}, \omega)$, of these structures and the possible enhancement of the electric field at various positions on the surface. For both quantities we first need to compute the reflection matrices, $\hat{R}(\mathbf{k}, \mathbf{k}'; \omega)$, defining scattering of the incoming wave into outgoing waves of momenta $\mathbf{k}'$. When dealing with ma-

terials whose dielectric response disperses strongly with frequency, such as graphite and silver, on-shell methods like the one developed in our group [10] are ideally suited to calculate these matrices. First we fix ω and hence $\epsilon(\omega)$ can be specified. By approximating the continuous fields by their values at a series of discrete points, we can construct the EM transfer matrix of our system. This transfer matrix, relating EM fields at one side of the structure to those on the other side in the y direction, allows us to calculate transmission and reflection coefficients for an incoming plane wave [10]. Once we have these matrices, the reflectance of the surface can be easily calculated:

$$R(\mathbf{k},\omega) = \sum_{\mathbf{k}'} |\hat{R}(\mathbf{k},\mathbf{k}';\omega)|^2, \qquad (1)$$

where the sum runs over only propagating outgoing waves.

In order to calculate the electric field surrounding the carbon nanotubes, we first construct the total $\mathbf{E}$ field outside the surface as a sum of the incident and reflected waves,

$$\mathbf{E}_{\text{total}}(\mathbf{r},\omega) = e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{E}_{inc}(\mathbf{k},\omega) \qquad (2)$$
$$+ \sum_{\mathbf{k}'} e^{i\mathbf{k}'\cdot r}\hat{R}(\mathbf{k},\mathbf{k}';\omega)\mathbf{E}(\mathbf{k}',\omega),$$

where $\mathbf{E}_{inc}(\mathbf{k},\omega)$ is the electric field associated with an incoming plane wave and $\mathbf{E}(\mathbf{k}',\omega)$ is the electric field associated with the outgoing plane wave $\mathbf{k}'$. In this case the sum runs over both propagating and evanescent waves. Then we integrate the EM fields in real space through the system to obtain a detailed picture of the electric field.

As we said above, multishell nanotubes are made of several concentric cylinders of planar graphite. Graphite is highly anisotropic and it is necessary to distinguish two different components, $\epsilon_\parallel(\omega)$ and $\epsilon_\perp(\omega)$, in its dielectric function for the directions parallel and normal to the axis, respectively. When transferring these dielectric functions to cylindrical geometry, for every point (x,y) inside the nanotube and outside the inner core we can write down a local dielectric tensor [11,12],

$$\hat{\varepsilon}(x,y,\omega) = \begin{pmatrix} \frac{x^2}{r^2}\varepsilon_\parallel + \frac{y^2}{r^2}\varepsilon_\perp & \frac{xy}{r^2}(\varepsilon_\parallel - \varepsilon_\perp) & 0 \\ \frac{xy}{r^2}(\varepsilon_\parallel - \varepsilon_\perp) & \frac{y^2}{r^2}\varepsilon_\parallel + \frac{x^2}{r^2}\varepsilon_\perp & 0 \\ 0 & 0 & \varepsilon_\perp \end{pmatrix}, \quad (3)$$

where $r = \sqrt{x^2 + y^2}$. For a point inside the inner core the local dielectric tensor is diagonal and equal to the dielectric function of silver, $\epsilon_{Ag}(\omega)$. For the calculations we show in this paper we have used the dielectric functions of graphite ($\epsilon_\parallel(\omega)$ and $\epsilon_\perp(\omega)$) and silver ($\epsilon_{Ag}(\omega)$), as tabulated in Ref. [13].

Very recently, an extension of the Transfer Matrix formalism described above has been developed [14], which is able to solve Maxwell equations with tensor-like dielectric functions like the one present in Eq. (3). This method has been applied with success [12] to explain the reported optical data of aligned carbon nanotube films [9]. Within this on-shell formalism it is possible to compute the reflection matrices needed to calculate the optical reflectance and the electric fields in real space.

The linear optical response of silver and other coinage metals is dominated by the surface plasmon resonance, ω_{sp}. For a nanometric particle, ω_{sp} depends on the plasma frequency of the metal, the dielectric surroundings and the particular geometry of the nanostructure. For an *isolated* metal cylinder in vacuum, the location of ω_{sp} is determined by the equation $\epsilon(\omega) + 1 = 0$ and the surface plasmon has a dipolar character. For the case of a silver cylinder $\omega_{sp} = 3.6$ eV. When nanoparticles are brought into close contact, electromagnetic coupling between them provokes a shift of ω_{sp} to lower energies and the dipolar surface plasmon converts into a localised one, trapped in the region between the nanostructures [2]. An incident plane wave of appropriate frequency can excite this surface plasmon, creating a huge $\mathbf{E}$ field at this location and leading to large reductions in optical reflectance at this frequency.

In Fig. 2 we show the optical reflectance for frequencies ranging from 1 to 4 eV, calculated for an array of close-packed carbon nanotubes filled with silver (see Fig.1). The diameter of the inner core, d_{in}, is varied between 3 and 9.5 nm. As shown in the figure, for $d_{in} \geq 5$ nm there is a dip in the frequency dependence of the optical reflectance. This is a clear signal that for these values of d_{in}, the incident photon is exciting surface plasmons associated with the silver cylinders filling the nanotubes. Plasmons of carbon are located at higher energies, 5.2 and 6.2 eV, and cannot be excited at these frequencies [12]. Moreover, the shift to lower energies of ω_{sp} as d_{in} is increased indicates that encapsulated silver nanostructures are electromagnetically coupled, their carbon shells serving as the medium for this interaction. We note that the silver surface plasmon is absent when d_{in} is less than 4 nm, just the minimum value of d_{in} at which a carbon nanotube can be filled with silver using capillary forces [7]. Another interesting conclusion that can be drawn from looking at this figure is that the shift to lower energies of ω_{sp} is accompanied by a narrowing of the plasmon linewidth. A narrow linewidth indicates that radiative coupling to the vacuum of the plasmon is weak, and therefore a huge enhancement of the optical fields is expected for the largest values of d_{in}.

It can be shown that for small values of d_{in} (5 or 6 nm) the dip in the frequency dependence of the optical reflectance is associated with excitation of a **dipolar** surface plasmon, similar to the one present in *isolated* silver cylinders. However, as the distance between the silver cylinders is reduced, the surface plasmon excited becomes more localised. In Fig. 3, we show a detailed picture of the $\mathbf{E}$ field generated by the incident photon for $d_{in} = 8$ nm. We have evaluated the fields at $w = 2.5$

eV, the frequency of minimum reflectance for this case (see Fig. 2). Clearly the incident radiation is exciting a very localised surface plasmon and the intensity of the **E** field is strongly enhanced with respect to the incident one. The electric field within the carbon shell is also large because at this range of frequencies carbon behaves effectively as a lossy dielectric. It is also worth mentioning that the induced charge (just the divergence of the **E** field shown in Fig. 3) is located not only on the surface of the silver cylinders but also within the carbon shell. This is due to the tensor-like character of the optical response of graphite that allows to fulfil the condition $\nabla \cdot (\hat{\varepsilon}\mathbf{E}) = 0$ with $\nabla \cdot \mathbf{E}$ different form zero not only at the interfaces but also inside the nanotubes. This *bulk* induced charge reinforces the intensity of the **E** field created by excitation of the silver surface plasmon.

These results demonstrate that the ability to enhance optical fields, inherent to silver nanostructures, is still present when they are encapsulated inside carbon nanotubes. However, as the surface plasmon strength depends on the diameter of the silver inner core, this capability is expected to be very sensitive to this diameter. In order to evaluate this enhancing property quantitatively, and investigate the possibility of using these surfaces as SERS active substrates, we have calculated the local enhancement of the Raman signal of a molecule absorbed in the region between the nanotubes. To a first approximation, this Raman signal depends on the fourth power of the total electric field at the molecule position $(\mathbf{E}(\mathbf{r}_m, \omega))$, and hence its enhancement due to the presence of the surface is simply:

$$\rho(\mathbf{r}_m, \omega) = \left| \frac{\mathbf{E}(\mathbf{r}_m, \omega)}{E_{\text{inc}}(\omega)} \right|^4, \tag{4}$$

where $\mathbf{r}_m$ represents the location of the molecule, and $E_{\text{inc}}(\omega)$ is the electric field associated with the incident plane wave.

In Fig. 4 this enhancement is shown, as a function of the incoming photon energy and for different values of d_{in}, ranging from 5 to 9.5 nm. As expected from dependence of the excited surface plasmon linewidth on d_{in}, enhancement grows rapidly from 10^4 for $d_{in} = 5$ nm to 10^6 for $d_{in} = 9.5$ nm. As d_{in} is increased, the induced charge is becoming more localised and, therefore, the **E** field in the region between the nanotubes is larger. This behaviour had previously been found when studying the optical response of silver nanoparticles deposited on a silver surface [2]. For comparison, we show in the same figure the expected enhancement of the Raman signal for an array of bare silver cylinders with diameters of 9.5 nm, their axis being separated by a distance of 10.3 nm. Due to the lossy characteristics of carbon at this range of frequencies, encapsulated silver nanostructures have a weaker enhancing capacity with respect to the bare ones. On the other hand, in the case of encapsulated tubes the dependence of the enhancement on

the energy of the incoming photon has a less pronounced resonant behaviour, and its value is large and practically constant at all frequencies within the visible range. This distinctive property of Ag-filled carbon nanotubes might be expected to be useful in practical applications.

In conclusion, we have investigated the optical response of carbon nanotubes filled with silver. We have shown how a silver nanostructure's ability to enhance optical fields is retained when it is encapsulated inside these tubes. For the largest values of inner core radius, the enhancement of the **E** field intensity can be as large as 10^3. The experimental viability of building up ordered structures made of these silver filled carbon tubes could open the possibility of using these systems as spectroscopic enhancers in the visible range. The optical properties of these structures could be tuned by varying the diameter of the inner core, carbon shells playing the role of moulds that avoid aggregation between the metal nanoparticles and fix their mutual separation. Standard SERS-active surfaces are well-known to be difficult to use in a controlled way, and encapsulated nanostructures can provide, therefore, a novel technique for the preparation of well-defined SERS-active substrates. Moreover, the capability of these systems to enhance optical fields can be used not only for spectroscopic purposes: if we shine a laser beam of appropriate frequency into a solution of Ag-filled carbon nanotubes, van der Waals attraction between the tubes can be greatly photo-enhanced and binding into 3D structures of Ag-filled carbon nanotubes can be facilitated.

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Figure Captions

Figure 1. Our model of an array of Ag-filled carbon nanotubes: the cylinders of outer diameter $d_{out} = 10$ nm are infinitely long in the z-direction and are distributed periodically in the x-direction with a separation of $d = 10.3$ nm. The inner core filled with silver will be varied between 3 and 9.5 nm in our calculations. We study the electromagnetic interaction of this structure with a normally incident *p-polarized* plane wave of momentum **k** and energy ω.

Figure 2. Calculated optical reflectance of the structure shown in Fig. 1 for a normally incident photon of frequency ranging from 1 to 4 eV, and different values of the inner core filled with silver, d_{in}.

Figure 3. A detailed picture of the total **E** field generated by a normally incident plane wave impinging on the array of Ag-filled carbon nanotubes of Fig. 1 with $d_{in} = 8$ nm. The **E** field is evaluated at $\omega = 2.5$ eV, the frequency at which the optical reflectance is minimum for this case. The total **E** field is shown for two unit cells of the array.

Figure 4. The local enhancement of the Raman signal evaluated at the region between the nanotubes, for different values of d_{in} and as a function of the energy of the incoming photon. The same quantity, as evaluated for bare Ag cylinders of diameter 9.5 nm and separated by 10.3 nm, is also shown.
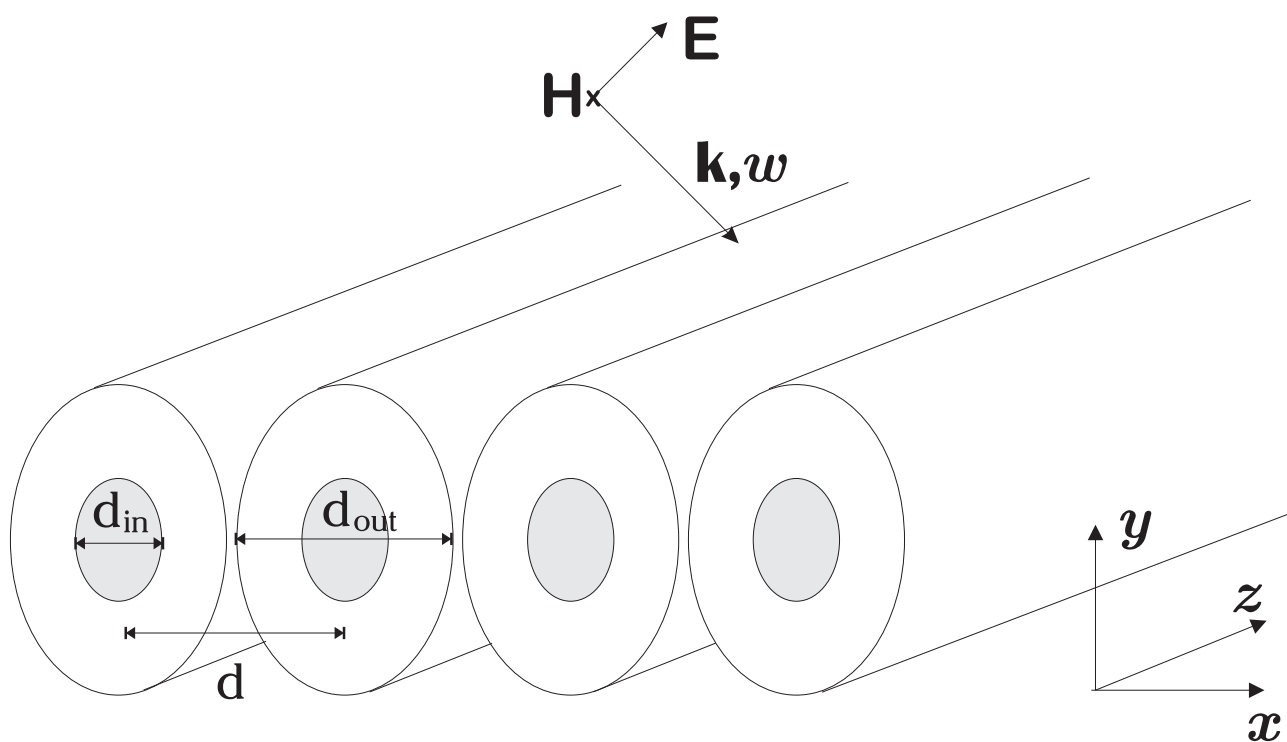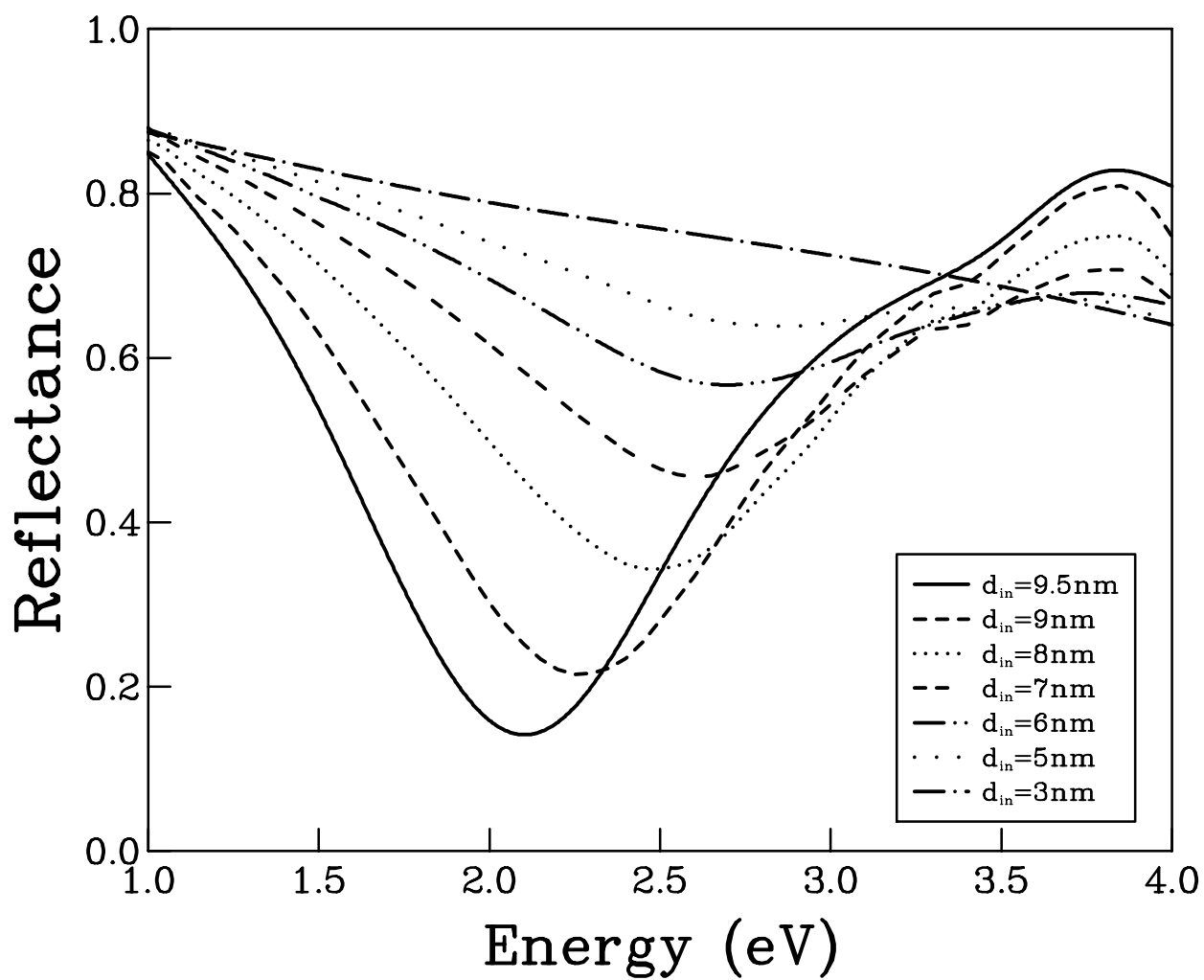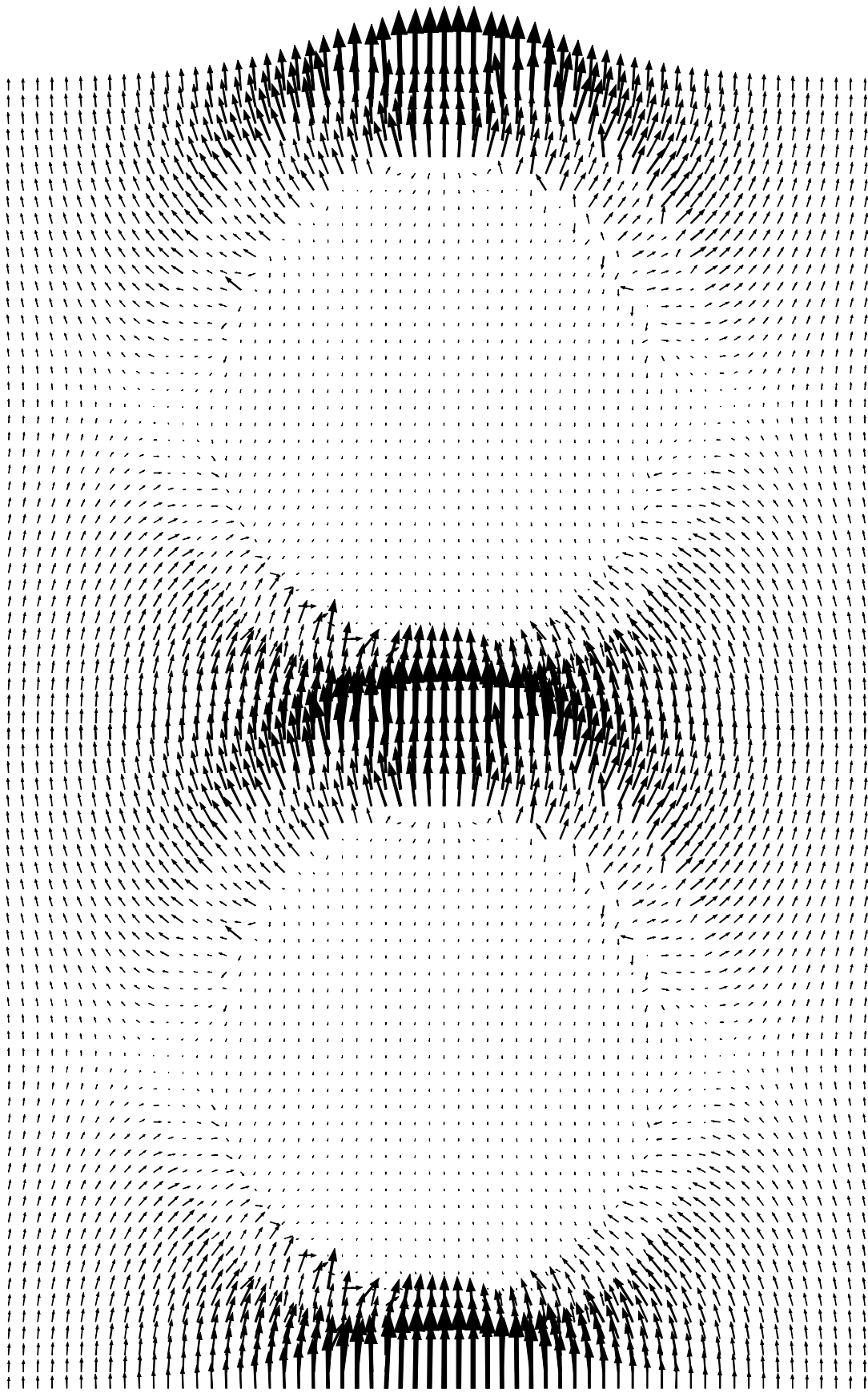
Figure 1

Figure 2

Figure 3

Figure 4